

Effect of Sodium Carbonate and Other Sodium Salts on Clay Minerals and the Clay Fraction of Soils

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In the course of alkali soil formation the micro-minerals present in the soil decompose or get transformed under the influence of soda and/or other sodium salts. These salts diminish soil fertility in two ways, viz.: first: they exert a detrimental effect on plant growth (in such cases the so-called "solonchak-formation" is decisive), and second: they bring about unfavourable changes in the physical properties of soils, for example soda and other sodium salts affect soil colloids. The consequence is the reduction of the adsorption capacity as well as that of the water and nutrient storage power of the soil. This is called the "solonetz-type" alkalization or, should the destruction of clay minerals in the upper soil horizon lead to the accumulation of silica, the "soloth"-forming process. There is also, the question of whether the sesquioxides, migrating in the soil, should be considered as indicators of the alkalization process.

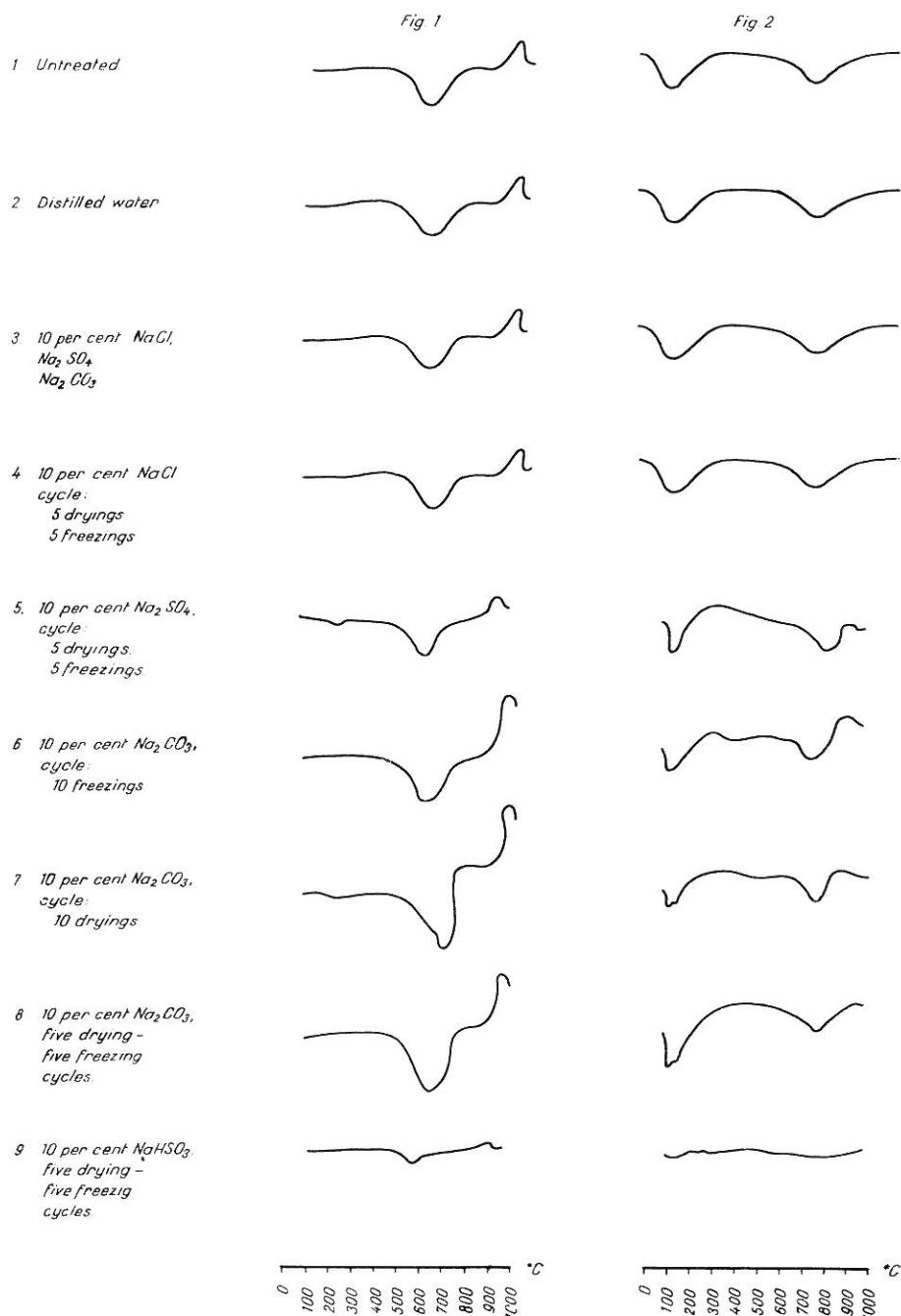
Thus, theoretical as well as practical aspects of soil alkalization point toward the high importance of studies concerning changes, transformation and/or decomposition of micro-minerals, in order to elucidate the nature of the pedological processes involved, and to understand the reasons for decreased fertility in such soils.

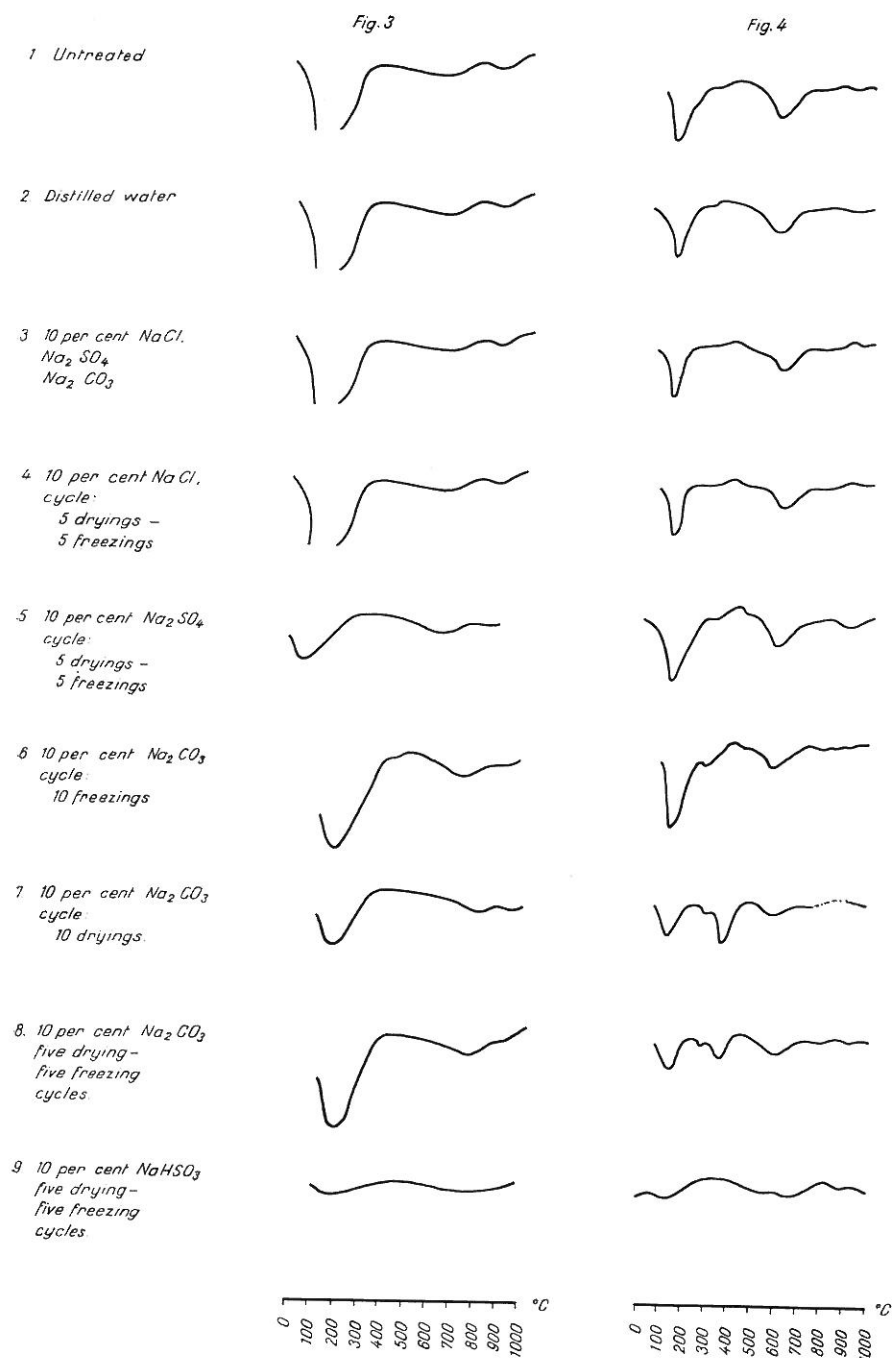
Experimental

In order to get a better understanding of the processes mentioned, 3 clay minerals belonging to different types and the clay (less than 0.001 mm) from the A-horizon of a strongly solonized meadow soil were subjected to treatments with distilled water and with solutions of NaCl, Na₂SO₄, Na₂CO₃ and NaHSO₃. The treatments were also combined with freezing or drying. All operations were repeated several times until considerable changes in the crystal lattices of the samples could be detected. For the sake of brevity in this paper only those thermograms and X-ray diffraction lines are given, which show the most characteristic changes observed in the course of treatment of a series of the similar samples.

Composition of the untreated samples:

1. *Kaolinite*. The DTA curve (Fig. 1., thermogram 1.) as well as the X-ray diffraction pattern indicates a typical specimen of kaolinite. Most characteristic are the lines 3.53, 3.32, 2.55, 2.47, 2.32, 1.47 Å etc.





2. *Illite*. The DTA curve (Fig. 2., thermogram 1.) and X-ray lines (4.47, 3.33, 2.69, 1.49 Å etc.) are characteristic of illite.

3. *Montmorillonite*. The DTA curve (Fig. 3., thermogram 1.) and the X-ray diffraction pattern 15.47, 4.47, 4.02, 2.57, 2.24 Å etc. indicate a typical montmorillonite specimen.

4. *The composition of the soil clay fraction was as follows*: On the DTA curve (Fig. 4., thermogram 1.) endothermic peaks between 100 and 200 °C, and about 600 °C, as well as the weak endothermic and exothermic effects beyond 900 °C, show the presence of illite and montmorillonite: the endothermic effect between 300 and 400 °C indicates sesquioxides. On the basis of the X-ray diffraction pattern (Table 1.) the sample contained illite and muscovite, but less quartz and montmorillonite. There were little sesquioxides in the sample.

Table 1.

Clay fraction of a strongly solonized meadow soil; A horizon, 0–5 cm.
Untreated

hkl	° J	hkl	° J	hkl	° J
5.30	very faint	2.360	medium strong	1.490	medium strong
4.49	faint	2.260	very faint	1.440	very faint
3.66	faint	2.110	medium strong	1.383	medium
3.46	very faint	1.986	medium strong	1.287	faint
3.31	strong	1.870	very faint	1.280	very faint
3.17	very faint	1.802	medium strong	1.220	very faint
2.96	very faint	1.688	medium faint	1.191	faint
2.82	faint	1.647	faint	1.175	faint
2.55	strong	1.528	medium strong	1.106	very faint
2.43	medium strong				

Treatments:

1. *Distilled water*. The samples were soaked in distilled water at room temperature for 1 week, then dried for 24 h at 105 °C. This cycle was repeated 10 times, following which a subsample was taken and analysed. Only the soil clay fraction indicated some loosening of the crystal structure after 10 treatment cycles (thermogram 4/2.), while the clay minerals were not affected (thermograms 1/2., 2/2. and 3/2.).

2. *10 per cent salt solutions*. The samples were soaked for 1 week in solutions of NaCl, Na₂SO₄ and Na₂CO₃, respectively. They were then dried by infrared irradiation and subjected to DTA and X-ray analyses. The X-ray diagrams and the DTA results showed no changes in the three clay minerals (thermograms 1/3., 2/3. and 3/3.), but a slight loosening of the crystal lattice was noticed with the soil clay fraction (thermogram 4/3.).

3. *Treatment with 10 per cent salt solutions in combination with freezing and drying*. After treating with the salt solutions mentioned above the samples were further treated in three different ways, viz.:

a) *Drying*. After soaking in the respective salt solution for a week at room temperature, the samples were dried for 24 h at 105 °C. These treatment

cycles were repeated from 1 to 10 times. After every cycle subsamples were taken and analysed.

b) *Freezing*. After soaking as above the samples were kept at -5°C for 24 h and then handled in the same way as after drying.

c) *Alternate drying and freezing*. After every two cycles subsamples were taken and examined.

A) *Treatment with 10 per cent solution of NaCl*. Only data obtained after 5 freezing and 5 drying cycles are given. With the three clay minerals neither X-ray diffraction nor DTA results (thermograms 1/4., 2/4. and 3/4.) showed any substantial change in the crystal structure. A slight loosening of the lattice was noticed in the case of the soil clay fraction (thermogram 4/4.).

B) *Treatment with 10 per cent solution of Na_2SO_4* . Only data obtained with 5 drying and 5 freezing cycles are given. Among the clay minerals the X-ray diagram of kaolinite showed no change but a slight loosening of the lattice was observed on the thermogram 1/5.). With illite and montmorillonite, however, the X-ray diagrams displayed a substantial effect on the crystal lattice. Instead of 15 lines with untreated substances only 8 were detected after the treatment, and in addition blackening of the background strongly increased. Also changes in the thermograms indicated loosening of the structure, especially at the exothermic and endothermic peaks (thermograms 2/5. and 3/5.).

Considerably greater changes were noticed on treatment of the soil clay fraction with Na_2SO_4 . Comparing the thermogram of the treated (4/5.), with that of the untreated (4/1.) sample a striking increase in the endothermic effect between 300 and 400 $^{\circ}\text{C}$, characteristic of sesquioxides and a considerable decrease in the endothermic effect at 600 $^{\circ}\text{C}$, characteristic of illite, could be observed. In contrast to the untreated sample the X-ray diffraction pattern indicated the presence of a newly-formed micro-mineral hydrargillite (lines at 1.98, 1.81, 1.74 and 1.64 \AA). At the same time number and intensity of lines pertaining to illite and muscovite decreased. Thus, decreases in the amounts of muscovite and illite and the appearance of hydrargillite in the sample could be demonstrated unequivocally.

C) *Treatment with 10 per cent Na_2CO_3 solution*. In this paper data given were obtained with

a) 10 freezings,

b) 10 dryings and

c) 5 and 5 alternating freezing and drying cycles. In the case of kaolinite only the DTA curve showed some loosening of the crystal lattice (thermograms 1/6., 1/7. and 1/8.). With illite and montmorillonite the blackening on the X-ray diagram and the reduction in line numbers from 15 to 8 showed the strong decrease in the degree of crystallization. With the latter two minerals the thermograms by changes at the peaks, proved loosening of structure (2/6., 2/7., 2/8., 3/6., 3/7. and 3/8.). The soil clay fraction displayed, in comparison with the clay minerals as well as with itself after Na_2SO_4 treatments, similar but considerably more distinct changes. After 10 freezings there was a flat endothermic peak on the DTA curve (thermogram 4/6.) at 300 $^{\circ}\text{C}$, indicating an increase in the amount of poorly crystallized hydrated iron oxide. The flattening of the endothermic peak about 600 $^{\circ}\text{C}$ proved the loosen

ing of the crystal lattice of illite. The double endothermic peaks between 300 and 400 °C, obtained with 10 dryings as well as with 5 to 5 alternating dryings and freezings (thermograms 4/7. and 4/8.) prove the presence of poorly crystallized goethite and the presence of hydrargillite. On examining the correlation of effects observed between 300 and 400 °C and the endothermic peak of illite at 600 °C it was found that after treatment

a) the endothermic peak of illite was flattened when the effect at 300 °C appeared (4/6.); while it almost completely disappeared after treatments

b) and *c)* when the double peak between 300 and 400 °C became visible (thermograms 4/7. and 4/8.). Thus, the DTA curve proved that illite decreased, hydrated iron oxides increased and hydrargillite appeared in the sample. The X-ray diffraction pattern showed subsequently for three treatment types a decrease in number and intensity of muscovite and illite lines (e.g. the 2.43 and 1.23 Å lines). At the same time the intensity of lines due to hydrated iron oxide (e.g. 2.25 Å) increased with all three treatment types. Treatments *b)* and *c)* induced the appearance of lines characteristic to hydrargillite (e.g. 1.89, 1.81, 1.74 and 1.70 Å). The relative amounts of illite and of muscovite thus decreased, while that of hydrated iron oxide increased in the sample under the effect of soda. After treatments *b)* and *c)* the formation of hydrargillite was also ascertained.

D) Treatment with 10 per cent solution of NaHSO₃. Data obtained with 5 drying and 5 freezing cycles are given. In consequence of the strong reducing effect of NaHSO₃ the DTA curves became almost completely flattened with all four samples, indicating the destruction of the crystal lattices (thermograms 1/9., 2/9., 3/9. and 4/9.). These statements were supported by the X-ray diffraction patterns showing the disappearance of numerous characteristic lines and an increase in basal blackening. Thus, the reducing agent exerted the most intensive influence observed on the samples.

Summary

The effects of water and solutions of NaCl, Na₂SO₄, Na₂CO₃ and NaHSO₃ on kaolinite, illite, montmorillonite and the clay fraction from the A horizon of a strongly solonized meadow soil were studied. The action of the solvents was combined with that of freezing and drying, all treatments being repeated several times.

The following results were obtained:

1. Comparing the effects on the crystal lattice exerted by distilled water and by salts such as Na₂CO₃, Na₂SO₄ and NaCl, it was found that Na₂CO₃ had the greatest, Na₂SO₄ a somewhat less vigorous, and NaCl and distilled water the weakest effect on the crystal lattices.

2. The most drastic effect was exerted by the reducing agent NaHSO₃, which caused complete destruction of crystals with all four samples.

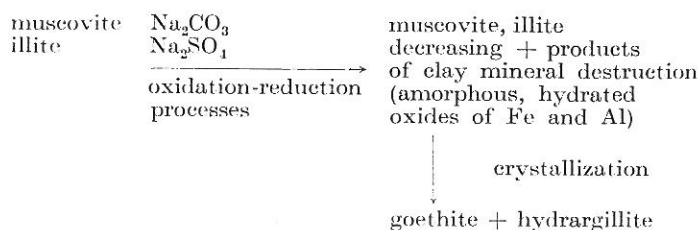
3. It is striking that, while 10 per cent solutions of soda and of sodium sulphate per se did not greatly affect the structure of crystal lattices, the same treatments combined with drying and/or freezing, especially when repeated several times, partially destroyed the micro-crystals. Thus it may be assumed that the dispersing action of sodium salts is increased by oxidation-reduction processes. This experience lends, from a micro-mineralogical point of view, strong support to the statement by SIGMOND, that the periodical alternation of excess moisture and drying out is a precondition of soil alkalization.

4. Of the minerals studied kaolinite was most stable, illite and montmorillonite were less stable, and the clay fraction of the soil was most subject to change. It is to be noted that the clay minerals in Hungarian solonchaks are mainly illite and montmorillonite. The stability of the clay fraction suggests that microminerals in soils generally decompose more readily than clay minerals in unaltered rocks.

5. The treatment of soil colloids with 10 per cent solutions of sodium sulphate or sodium carbonate lead in the case of all three treatment types (viz. 10 freezings, 10 dryings and 5 dryings-5 freezings, respectively) to a substantial decomposition of illite and muscovite, while the sesquioxide content of the samples increased markedly. This process was more intense with soda than with sodium sulphate. Thus, it may be assumed that migrating sesquioxides come, partly at least, from decomposing micro-minerals.

6. In the course of the above treatments with all six of them a new clay mineral appeared, which was not present in the original sample. This was hydrargillite. This mineral probably originated from amorphous aluminium oxide present in the clay fraction.

7. It may be ascertained in vitro that among conditions similar to those of alkali soil formation (periodic excess of moisture alternating with drying out, temperature changes characteristic to arid climates, accumulation of soda and of sodium sulphate in the soil solution) the following micromineralogical processes take place:



Thus, it is proposed that the decomposition of clay minerals in alkaline medium is followed by formation of new microminerals, when soil alkalization processes occur in nature.

Влияние соды и других солей натрия на глинистые минералы и коллоидную фракцию почвы

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Резюме

В этой работе автор занимается изучением микроминералогических процессов, происходящих под влиянием соды и других натриевых солей при образовании засоленных почв.

Каолинит, иллит, монтмориллонит и коллоидная фракция сильно солонцеватой луговой почвы обрабатывались дистиллированной водой и растворами NaCl , Na_2SO_4 , Na_2CO_3 , NaHSO_4 . Обработки растворами комбинировали с высушиванием и замораживанием, что повторялось несколько раз.

В результате исследований пришли к следующим выводам:

1. Сравнивая влияние обработок с растворами, встречающихся в почве солей Na_2CO_3 , Na_2SO_4 , NaCl и дистиллированной водой установили, что при одинаковых прочих условиях самое большое влияние на структуру кристаллической решетки оказывает Na_2CO_3 , слабее влияет Na_2SO_4 и самое незначительное влияние оказывают NaCl и дистиллированная вода.

2. Самый высокий эффект наблюдался при обработке редуцирующим раствором NaHSO_4 , в результате чего во всех четырех образцах произошло полное разрушение кристаллов.

3. При обработке 10% раствором соды или сульфата натрия существенных изменений в структуре кристаллической решетки не наблюдалось, в то же время обработка солевыми растворами тех же концентраций, но при высушивании и замораживании образцов, повторенных несколько раз, приводит к частичному разрушению микрокристаллов. Этот факт позволяет заключить, что диспергирующее влияние натриевых солей

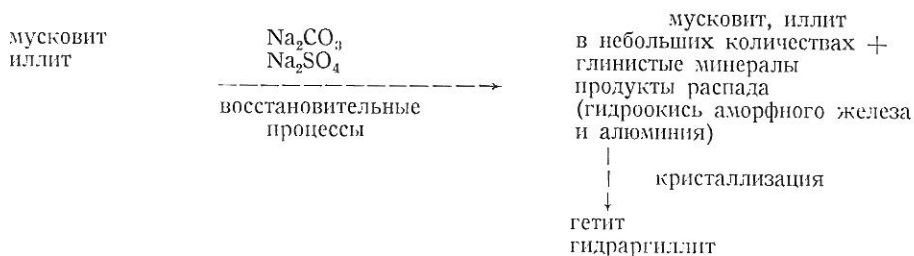
проявляется совместно с восстановительными процессами. Этот опыт с микроминералогической точки зрения подтверждает высказывания Зигмонда о том, что среди предпосылок, вызывающих засоление почв, периодическое переувлажнение и высыхание играют значительную роль.

4. При различных обработках наиболее стабильным оказался каолинит, менее стабильными иллит и монтмориллонит и наиболее изменчивой была коллоидная фракция почвы. Необходимо отметить, что в солонцах Венгрии среди глинистых минералов встречаются иллит и монтмориллонит. Способность к разрушению коллоидной фракции приводит к тому, что микроминералы почвы более подвержены разрушению, чем микроминералы, происходящие из чистых горных пород.

5. Обработка почвенных коллоидов 10% растворами сульфата и карбоната натрия, во всех трех вариантах обработки (десятикратное замораживание, десятикратное высушивание и 5-кратное высушивание-замораживание) приводит к разрушению большей части, находящихся в образцах, иллита и мусковита и увеличению содержания полуторных оксидов. В этом процессе сода играет более значительную роль, чем сульфат натрия. Эти факты говорят о том, что подвижные полуторные оксиды получаются главным образом в результате распада микроминералов.

6. В результате вышеупомянутых обработок (все шесть вариантов) обнаружили микроминерал гидрагиллит, которого не было в исходном образце. По всей вероятности микрокристаллы гидрагиллита возникают из окиси алюминия, находящейся в коллоидной фракции.

7. Опыты показали, что при образовании засоленных почв в одних и тех же условиях (периодическое переувлажнение, сменяющееся высыханием, изменение температур, характерное для аридных условий, увеличение количества соды и сульфата натрия в почвенном растворе) протекают следующие микроминералогические процессы:



Таким образом можно сказать, что разрушение микроминералов в щелочной среде и образование новых микрокристаллов, прошедших аморфную стадию, является одной из существенных сторон образования засоленных почв в природе.